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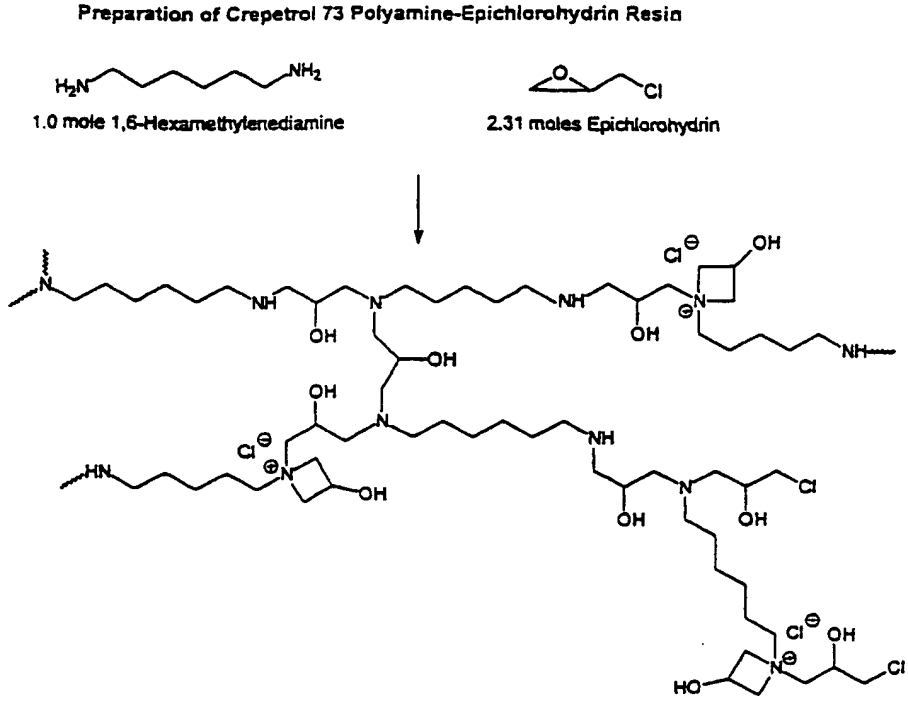
(54) Title: CREPING ADHESIVES



(57) Abstract: Creping adhesives, and methods for making and using them in the creping of cellulosic fiber webs. The creping adhesives are a combination of polyamine-epihalohydrin and poly(vinyl alcohol). The method comprises the preparation and application of the creping adhesives to attain strong adhesion of fiber webs onto a drying surface, and the creping of the fiber webs to obtain a soft, bulky tissue paper web.

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Combinations of PVOH with thermosetting, cationic polyamide resins have been used as creping adhesive compositions. Such combinations are disclosed in U.S. Patent No. 4,501,640 to Soerens for a creping adhesive comprising (1) an aqueous mixture of PVOH; and (2) a water-soluble, thermosetting cationic polyamide resin which provide increased adhesion in the manufacture of creped wadding.

U.S. Patent No. 4,528,316 to Soerens discloses an aqueous adhesive comprising water, PVOH and a water-soluble, cationic polyamide which is phase compatible with the PVOH. The polyamide of Soerens is the reaction product of a saturated aliphatic acid such as adipic acid, and a polyalkylene polyamine such as diethylene triamine which is further reacted with epichlorohydrin to yield the water-soluble, cationic polyamide. Furthermore, the adhesive of Soerens is used to adhere tissue to a creping cylinder in the manufacture of creped wadding.

U.S. Patent No. 4,684,439 to Soerens also discloses a wettable creping adhesive comprising an aqueous admixture of PVOH and water-soluble, thermoplastic polyamide resin. The resin is the reaction product of a polyalkylene polyamine, a saturated aliphatic dibasic carboxylic acid, and a poly(oxyethylene)diamine.

U.S. Patent No. 4,788,243 to Soerens discloses a creping adhesive comprising PVOH and a water-soluble, thermoplastic polyamide resin. The resin of Soerens is phase-compatible with PVOH and comprises the reaction product of polyalkylene polyamine, a saturated aliphatic dibasic carboxylic acid, and poly(oxyethylene)diamine. Additionally, U.S. Patent No. 5,865,950 to Vinson et al. discloses a method for dry creping tissue paper comprising the application of creping adhesives comprising PVOH and a water-soluble, thermosetting, cationic polyamide resin in at least two steps.

Furthermore, U.S. Patent No. 5,490,903 to Chen et al. discloses a creping adhesive composition comprising ethoxylated acetylenic diol. The creping adhesive composition of Chen et al. is said to be useful for creping through-dried tissue webs.

Polyamine-epihalohydrin resins have been widely used in paper production [H.H. Espy, in "Wet Strength Resins and Their Application", L.L. Chan, Ed., pp. 21-22, TAPPI Press, Atlantic GA (1994)]. Polyamine-epihalohydrin resins differ from polyamidoamine-epichlorohydrin resins by the lack of amide linkages. This lack of amide linkages makes

hydrohalide salt of a polyamine is condensed with an epihalohydrin to provide improved wet and dry strength to cellulosic substrates.

Further, compositions and methods of using polyamine-epihalohydrin resins as creping adhesive are disclosed in U.S. Patent No. 5,660,687 to Allen et al. in which a composition comprising polyamine-epihalohydrin resin creping adhesive and a creping release agent are applied together or separately in the creping process. U.S. Patent No. 5,833,806 to Allen et al. also discloses a method for creping fibrous webs comprising the application of a polyamine-epihalohydrin creping adhesive.

Despite many attempts to produce different kinds of creping adhesives, there still remains a need in the art for creping adhesives which provide improved adhesion. The present invention provides strong creping adhesives which may be used in the creping process.

SUMMARY OF THE INVENTION

The present invention relates to creping adhesives and methods of making and using such adhesives for creping tissue paper. The creping adhesives of the present invention include polyamine-epihalohydrin resin and PVOH, and are useful in the manufacture of soft, absorbent paper webs.

The present invention is directed to creping adhesives comprising polyamine-epihalohydrin resin and polyvinyl alcohol, and methods of their production and use for creping paper webs.

In particular, the present invention is advantageous in providing strong adhesion of the cellulosic fiber web to the dryer surface during the creping process to attain a soft, bulky tissue paper web.

The present invention provides a creping adhesive composition comprising polyamine-epihalohydrin and polyvinyl alcohol, wherein the polyamine-epihalohydrin resin is the reaction product of an epihalohydrin and a polyamine, the polyamine has the following formula:

$$H_2N\text{-}A\text{-}H,$$

wherein A is $[CHZ\text{-}(CH_2)_n\text{-}NR\text{-}]_x$ or $[CH_2\text{-}(CHZ)_m\text{-}(CH_2)_n\text{-}NR\text{-}]_x$,

Still further, the concentration of solids in the aqueous solution of the present invention is from about 0.01% to about 10% solids, preferably from about 0.2% to about 5%, and most preferably from about 0.1% to about 2.5%.

The fraction of polyamine-epihalohydrin resin present in the solids is from about 5% to about 95%, preferably from about 7.5% to about 92.5%, and most preferably from about 10% to about 90% by weight.

The fraction of polyvinyl alcohol present in the solids is from about 95% to about 5%, preferably from about 92.5% to about 7.5%, and most preferably from about 90% to about 10% by weight.

Still even further, the polyamines of the present invention include polyalkylene, polyaralkylene, polyalkarylene, or polyarylene amines. The polyaralkylene amines comprises 1-phenyl-2,4-pentane diamine, or 2-phenyl-1,3-propanediamine. The polyarylene amines comprises phenylene diamine. The polyalkylene amines comprises ethylenediamine (EDA), bishexamethylenediamine (BHMT), hexamethylenediamine (HMDA), diethylenetriamine (DETA), triethyleneteramine (TETA), tetraethylenepentamine (TEPA), dipropylenetriamine (DPTA), tripropyleneteramine (TPTA), tetrapropylenepentamine (TPPA), N-methyl-bis-(aminopropyl)amine (MBAPA), spermine or spermidine.

Even further, the present invention comprises epihalohydrin such as epicholorohydrin, epibromohydrin or epiiodohydrin.

In addition, the creping composition of the present invention may be in a form comprising at least one of aqueous, solid, dispersion, and aerosol.

Also, the method of the present invention comprises the simultaneous or individual application of a polyamine-epihalohydrin resin and a polyvinyl alcohol to a drying surface or paper web.

The present invention provides a method of creping cellulosic fiber webs which comprises the step of applying a creping adhesive to a drying surface, the creping adhesive comprising polyamine-epihalohydrin resin and polyvinyl alcohol.

According to the invention, the cellulosic fiber web may be adhered to the drying surface of a Yankee Dryer. The dry cellulosic fiber web is then creped from the drying surface with a creping instrument such as a doctor blade.

The present invention is directed to creping adhesives possessing strong adhesion properties. The creping adhesive compositions of the present invention are obtained from a combination of polyamine-epihalohydrin resin and PVOH. Creping adhesives having such combinations can improve the performance of the creping process in the production of paper webs, particularly when used in the through-air-dried process. Further, the creping adhesive compositions of the present invention can enhance the binding of cellulosic fiber webs onto the drying surface and provide softer paper webs.

The creping adhesives of the present invention provide strong adhesion to cellulosic fiber webs and are advantageous over adhesion compositions in the art using polyamidoamine-epihalohydrin resins. The lack of amide linkages in the polymer backbone makes the polyamine-epihalohydrin resins less susceptible to degradation by hydrolysis in comparison to polyamidoamine-epihalohydrin resins. Also, the higher level of branching observed in polyamine-epihalohydrin in comparison to the polyamidoamine-epihalohydrin resins, has a strong effect on the polymer's physical, mechanical and rheological properties.

As used herein, the term "web" refers to paper products including tissue paper or paper towels.

As used herein, the terms "cellulosic fiber web, fibrous web, tissue paper web, paper web, web and cellulosic fiber product" all refer to sheets of paper made by a process which comprises forming a papermaking furnish, depositing the furnish onto a foraminous surface, removing water from the web, and the steps of adhering the sheet to a drying surface such as a Yankee Dryer and removing the sheet by a creping blade such as a doctor blade.

The creping process of the present invention can include the steps of applying the presently claimed creping adhesive to a drying surface to provide a fibrous web, adhering the web to the drying surface by pressing the fibrous web against said surface, and creping the fibrous web with a creping device to dislodge it from the drying surface. The creping adhesive of the present invention can also be applied to the fibrous web in the creping process.

The present invention also pertains to a process of creping paper. The creping process of the present invention can comprise the steps of providing a fibrous web, and creping this web. The creping process can be accomplished by applying a creping

The polyamine-epihalohydrin resin present in the creped tissue paper web is from about 0.0001% to about 5%, preferably from about 0.0005% to about 1%, and most preferably from about 0.001% to about 0.5% by weight based on paper.

The PVOH present in the creped tissue paper web is from about 0.0001% to about 5%, preferably from about 0.0005% to about 1%, and most preferably from about 0.001% to about 0.5% by weight based on paper.

The application of creping adhesives of the present invention can be done in any manner known in the art and in forms comprising aqueous, solid, dispersion or aerosol. One preferred mode of application is via a spray boom directed at the surface of the drying surface prior to transfer of the paper web. The creping adhesives can also be added at the wet end of the paper machine or can be applied to the wet web prior to its contact with the surface. Spray application of the creping adhesive can be done according to any of the conventional methods known in the art or any desired combination of application procedures. The order of addition of the creping adhesive comprising polyamine-epihalohydrin resin and PVOH can be varied. The methods of application comprise simultaneous or individual application of the polyamine-epihalohydrin resin and PVOH to a drying surface or web to form the creping adhesive.

As used herein, the term "solids" refers to the materials that are the active components or active ingredients of the present invention. The creping adhesives of the present invention are present in an aqueous solution with a solids content of polyamine-epihalohydrin resin and PVOH.

The concentration of solids in the aqueous solution is from about 0.01% to about 10.0% solids, preferably from about 0.2% to about 5.0% solids, and most preferably from about 0.1% to about 2.5% solids.

The fraction of polyamine-epihalohydrin present in the solids is from about 5.0% to about 95.0%, preferably from about 7.5% to about 92.5%, and most preferably from about 10% to about 90% by weight.

The fraction of PVOH present in the solids is from about 95% to about 5.0%, preferably from about 92.5% to about 7.5%, and most preferably from about 90.0% to about 10.0% by weight.

wherein A is $[CHZ-(CH_2)_n-NR-]_X$ or $[CH_2-(CHZ)_m-(CH_2)_n-NR-]_X$,

when A is $[CHZ-(CH_2)_n-NR-]_X$, n = 1 to 7, x = 1 to 6, R = H or CH_2Y, Z = H or CH_3, and Y = CH_2Z, H, NH_2, or CH_3,

when A is $[CH_2-(CHZ)_m-(CH_2)_n-NR-]_X$, m = 1 to 6, n = 1 to 6, m+n = 2 to 7,R = H or CH_2Y, Z = H or CH_3, and Y = CH_2Z, H, NH_2, or CH_3,

and mixtures thereof.

The preferred polyalkylene polyamines include bishexamethylenetriamine, hexamethylenediamine, and mixtures thereof.

The epihalohyrin of the present invention can include epichlorohydrin, epibromohydrin or epiiodohydrin. The preferred epihalohydrin includes epichlorohydrin.

The polyamine-epihalohydrin resins of the present invention comprise the water-soluble polymeric reaction product of epihalohydrin and polyamine. In making Daniel's Resins, the polyamine is added to an aqueous mixture of the epihalohydrin so that during addition, the temperature range is less than or equal to 60 °C. Preferably, the temperature range is from about 25 °C to about 60 °C. Most preferably, the temperature range is from about 30 °C to about 45 °C. Lower temperatures lead to further improvements, however, too low a temperature can build dangerously latent reactivity into the system.

Alkylation of the polyamine occurs rapidly to form secondary and tertiary amines depending on the relative amounts of epihalohydrin and polyamine. The levels of epihalohydrin and polyamine are such that between about 50% and 100% of the available amine nitrogen sites are alkylated to tertiary amines. Excess epihalohydrin beyond that required to fully alkylate all the amine sites to the tertiary amine is less preferred because this results in increased production of epihalohydrin byproducts.

Following complete addition of the polyamine, the temperature of the mixture is allowed to rise and/or the mixture is heated to effect crosslinking and azetidinium formation. The crosslinking rate is a function of concentration, temperature, agitation , and the addition conditions of the polyamine, all of which can be readily determined by those skilled in the art. The crosslinking rate can be accelerated by the addition of small shots of the polyamine or other polyamines of the present invention or addition of various alkalines at or near the crosslinking temperature. The resin can be stabilized against

mixture is then heated to approximately 85°C until a Gardner-Holt viscosity of "S" to "T" is achieved. At this point, water is added to bring the solids level to about 46% and the temperature is adjusted to approximately 76°C. The temperature is maintained at this point until a Gardner-Holt viscosity of "T" to "U" is achieved. Heating is discontinued and concentrated sulfuric acid and water are added to the reaction to bring the solids level to about 38%. After cooling to below approximately 35°C, the pH is then adjusted to about 2.75 with concentrated sulfuric acid.

Other polyamine-epihalohydrin resins of the present invention may be prepared as described above.

Example 2

Polyamine-epihalohydrin resin of this example is prepared as described in Example 1. The polyamine-epihalohydrin resin is prepared from 1 mole of 1,6-hexamethylenediamine and 2.31 moles of epicholorohydrin. The resulting hexamethylenediamine-epichlorohydrin resin is a highly branched, irregular structure that contains a number of different functional groups. These include secondary alcohol, secondary amine, tertiary amine, azetidinium chloride and aminochlorohydrin. The resulting polyamine-epihalohydrin resin is shown in Figure 1 having a highly branched structure.

Example 3

A series of samples (Sample Nos. 8-11, 16-19 and 21-24) containing various PVOH, polyamine-epihalohydrin resins, and mixtures thereof are shown in Figure 2. In Figure 2, Airvol 523, Airvol 540 and Airvol 425 manufactured by Air Products and Chemicals, Inc. (Allentown, PA) and are various grades of PVOH used in this example. Airvol 523 and Airvol 540 are partially hydrolyzed PVOH products (degree of hydrolysis = 87.0-89.0%). The weight average molecular weight of Airvol 523 is in the range of 85,000-146,000 Daltons while the weight average molecular weight of Airvol 540 is between 124,000 and 186,000 Daltons. Airvol 425 is a PVOH product having an intermediate level of hydrolysis (95.5-96.5%) and a weight average molecular weight in the range of 85,000 to 150,000 Daltons. Crepetrol 73 which is

the applied force. This normalization is accomplished by multiplying the adhesion value by [10/(Applied force in kg)]. The paper which is used for testing is a 40 lb basis weight sheet that is prepared from a 70/30 hardwood/softwood bleached Kraft furnish.

The results of the adhesive testing are illustrated in Figure 2.

Figure 2 shows a comparison of the adhesion capability of creping adhesives of the present invention containing polyamine-epihalohydrin, and comparable samples containing polyamidoamine-epihalohydrin. Various grades of PVOH are combined with the samples of the presention invention and comparative samples. Sample nos. 8-11 of the present invention in combination with Airvol 540, demonstrate a higher level of adhesion than the comparative sample nos. 4-7. Similarly, sample nos. 16-19 of the present invention which are combined with Airvol 425, show a higher level of adhesion than the comparative sample nos. 13-15. Further, sample nos. 21-24 of the present invention in combination with Airvol 523, show a similar level of adhesion as sample nos. 8-11 which are combined with Airvol 540.

The results from Figure 2 show creping adhesives of the present invention demonstrate stronger adhesion in comparison to comparable creping adhesives.

Adhesion testing of the Crepetrol 73-PVOH formulations is further depicted in Figure 3. The samples of Crepetrol 73-PVOH are prepared as described in Example 1, and the testing for creping adhesion is performed as described above. Varying concentrations of PVOH are shown from 0 to 100%. The concentration of Crepetrol 73 also varies according to the amount of PVOH present, so that the combination of both in the mixture equals to 100%. The level of adhesion for creping adhesive combinations of Crepetrol 73-Airvol 523, Crepetrol 73-Airvol 540 and Crepetrol 73-Airvol 425 demonstrate high levels of adhesion over a wide range of compositions.

Example 4

Production of Tissue Paper

A 0.5% solids aqueous solution of creping adhesive is sprayed onto the surface of a Yankee Dryer along with the appropriate amount of release agent to provide a good balance of adhesion and release. This application optimizes both the productivity

What is claimed is:

1. A method of creping cellulosic fiber webs which comprises the step of applying a creping adhesive to a surface, the creping adhesive comprising polyamine-epihalohydrin resin and poly(vinyl alcohol).

2. The method of claim 1, wherein the creping adhesive comprises the reaction product of polyamine-epihalohydrin poly(vinyl alcohol).

3. The method of claim 1, wherein the ratio by weight of polyamine-epihalohydrin resin:poly(vinyl alcohol) is a range from about 99:1 to 1:99.

4. The method of claim 3, wherein the ratio by weight of polyamine-epihalohydrin resin:poly(vinyl alcohol) is a range from about 95:5 to 5:95.

5. The method of claim 4, wherein the ratio by weight of polyamine-epihalohydrin resin:poly(vinyl alcohol) is a range from about 90:10 to 10:90.

6. The method of claim 1, wherein the polyamine-epihalohydrin resin is from about 0.0001% to about 5% by weight based on paper.

7. The method of claim 6, wherein the polyamine-epihalohydrin resin is from about 0.0005% to about 1% by weight based on paper.

8. The method of claim 7, wherein the polyamine-epihalohydrin resin is from about 0.001% to about 0.5% by weight based on paper.

9. The method of claim 1, wherein the poly(vinyl alcohol) is from about 0.0001% to about 5% by weight based on paper.

18. The method of claim 1, wherein the creping adhesive is in a solids aqueous solution.

19. The method of claim 18, wherein the concentration of creping adhesive in an aqueous solution is from about 0.01% to about 10% solids.

20. The method of claim 18, wherein the concentration of creping adhesive in an aqueous solution is from about 0.2% to about 5% solids.

21. The method of claim 18, wherein the concentration of creping adhesive in an aqueous solution is from about 0.1% to about 2.5% solids.

22. The method of claim 18, wherein the solids comprises a fraction of polyamine-epihalohydrin resin from about 5% to about 95%.

23. The method of claim 22, wherein the solids comprises a fraction of polyamine-epihalohydrin resin from about 7.5% to about 92.5%.

24. The method of claim 23, wherein the solids comprises a fraction of polyamine-epihalohydrin resin from about 10% to about 90%.

25. The method of claim 18, wherein the solids comprises a fraction of poly(vinyl alcohol) from about 95% to about 5%.

26. The method of claim 25, wherein the solids comprises a fraction of poly(vinyl alcohol) from about 92.5% to about 7.5%.

27. The method of claim 26, wherein the solids comprises a fraction of poly(vinyl alcohol) from about 90% to about 10%.

36. The method of claim 33, wherein the reaction product of epihalohydrin and polyamine is formed at a temperature from about 30°C to about 45°C.

37. The method of claim 1, wherein the polyamine of the polyamine-epihalohydrin resin comprises polyalkylene, polyaralkylene, polyalkarylene, or polyarylene.

38. The method of claim 37, wherein the polyalkylene comprises ethylenediamine (EDA), bishexamethylenediamine (BHMT), hexamethylenediamine (HMDA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), dipropylenetriamine (DPTA), tripropylenetetramine (TPTA), tetrapropylenepentamine (TPPA), N-methyl-bis-(aminopropyl)amine (MBAPA), spermine or spermidine.

39. The method of claim 37, wherein the polyaralkylene comprises 1-phenyl-2,4-pentane diamine, or 2-phenyl-1,3-propanediamine.

40. The method of claim 37, wherein the polyarylene comprises phenylene diamine.

41. The method of claim 1, wherein the epihalohydrin of the polyamine-epihalohydrin resin comprises epicholorohydrin, epibromohydrin or epiiodohydrin.

42. The method of claim 1, wherein the surface comprises a cellulosic fiber web.

43. The method of claim 1, wherein the surface comprises the drying surface of a Yankee Dryer.

44. The method of claim 43, wherein a cellulosic fiber web is adhered to the drying surface.

45. The method of claim 44, wherein the dry cellulosic fiber web is creped from the drying surface with a creping instrument.

56. The composition of claim 48, wherein the poly(vinyl alcohol) is from about 0.0001% to about 5% by weight based on paper.

57. The composition of claim 56, wherein the poly(vinyl alcohol) is from about 0.0005% to about 1% by weight based on paper.

58. The composition of claim 57, wherein the poly(vinyl alcohol) is from about 0.001% to about 0.5% by weight based on paper.

59. The composition of claim 48, wherein the polyamine-epihalohydrin resin added to the creping adhesive has a molecular weight in a range from about 500 to about 1,000,000 Daltons before addition to form the adhesive.

60. The composition of claim 59, wherein the polyamine-epihalohydrin resin added to the creping adhesive has a molecular weight in a range from about 2,500 to about 500,000 Daltons before addition to form the adhesive.

61. The composition of claim 60, wherein the polyamine-epihalohydrin resin added to the creping adhesive has a molecular weight in a range from about 5,000 to about 250,000 Daltons before addition to form the adhesive.

62. The composition of claim 48, wherein the poly(vinyl alcohol) added to the creping adhesive has a molecular weight in a range from about 10,000 to about 1,000,000 Daltons before addition to form the adhesive.

63. The composition of claim 62, wherein the poly(vinyl alcohol) added to the creping adhesive has a molecular weight in a range from about 20,000 to about 500,000 Daltons before addition to form the adhesive.

74. The composition of claim 73, wherein the solids comprises a fraction of poly(vinyl alcohol) from about 90% to about 10%.

75. The compositon of claim 48 wherein the polyvinyl alcohol has a degree of hydrolysis range from about 80% to about 99%.

76. The composition of claim 75 wherein the polyvinyl alcohol has a degree of hydrolysis range from about 85% to about 99%.

77. The composition of claim 76 wherein the polyvinyl alcohol has a degree of hydrolysis range from about 87% to about 98%.

78. The composition of claim 48, wherein the polyamine-epihalohydrin resin is the reaction product of an epihalohydrin and a polyamine,

the polyamine has the following formula:

$$H_2N\text{-}A\text{-}H,$$

wherein A is $[CHZ\text{-}(CH_2)_n\text{-}NR\text{-}]_x$ or $[CH_2\text{-}(CHZ)_m\text{-}(CH_2)_n\text{-}NR\text{-}]_x$,

when A is $[CHZ\text{-}(CH_2)_n\text{-}NR\text{-}]_x$, n = 1 to 7; x = 1 to 6; R = H or CH_2Y; Z = H or CH_3; and Y = CH_2Z, H, NH_2, or CH_3, and

when A is $H_2N\text{-}[CH_2\text{-}(CHZ)_m\text{-}(CH_2)_n\text{-}NR\text{-}]_x$, m = 1 to 6; n = 1 to 6; m+n = 2 to 7; R = H or CH_2Y, Z = H or CH_3; and Y = CH_2Z, H, NH_2, or CH_3.

79. The composition of claim 78, wherein the reaction product of epihalohydrin and polyamine is formed at a temperature less than or equal to 60°C.

80. The composition of claim 78, wherein the reaction product of epihalohydrin and polyamine is formed at a temperature from about 25°C to about 60°C.

81. The composition of claim 78, wherein the reaction product of epihalohydrin and polyamine is formed at a temperature from about 30°C to about 45°C.

91. The method of claim 90, wherein the by weight of polyamine-epihalohydrin resin:poly(vinyl alcohol) is a range from about 90:10 to 10:90.

92. The method of claim 87, wherein the creping adhesive is in a solids aqueous solution.

93. The method of claim 92, wherein the concentration of creping adhesive in an aqueous solution is from about 0.01% to about 10% solids.

94. The method of claim 93, wherein the concentration of creping adhesive in an aqueous solution is from about 0.2% to about 5% solids.

95. The method of claim 94, wherein the concentration of creping adhesive in an aqueous solution is from about 0.1% to about 2.5% solids.

96. The method of claim 92, wherein the solids comprises a fraction of polyamine-epihalohydrin resin from about 5% to about 95%.

97. The method of claim 96, wherein the solids comprises a fraction of polyamine-epihalohydrin resin from about 7.5% to about 92.5% by weight.

98. The method of claim 97, wherein the solids comprises a fraction of polyamine-epihalohydrin resin from about 10% to about 90% by weight.

99. The method of claim 92, wherein the solids comprises a fraction of poly(vinyl alcohol) from about 95% to about 5%.

100. The method of claim 99, wherein the solids comprises a fraction of poly(vinyl alcohol) from about 92.5% to about 7.5%.

INTERNATIONAL SEARCH REPORT

Inte ional Application No
PCT/US 00/31080

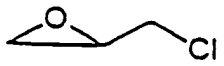
C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 129 528 A (PETROVICH JOHN P ET AL) 12 December 1978 (1978-12-12) cited in the application	

FIGURE 1

Preparation of Crepetrol 73 Polyamine-Epichlorohydrin Resin

1.0 mole 1,6-Hexamethylenediamine



2.31 moles Epichlorohydrin

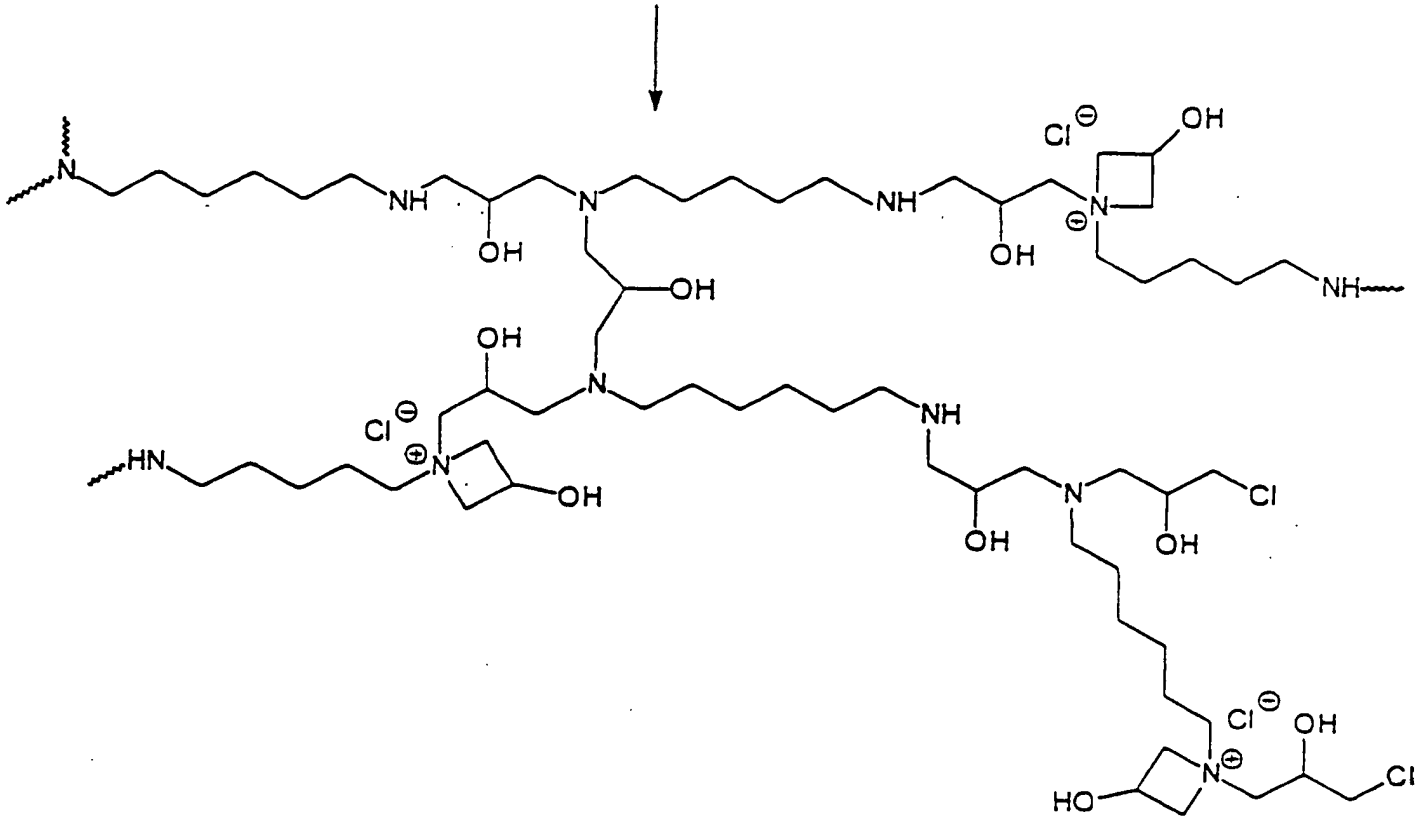
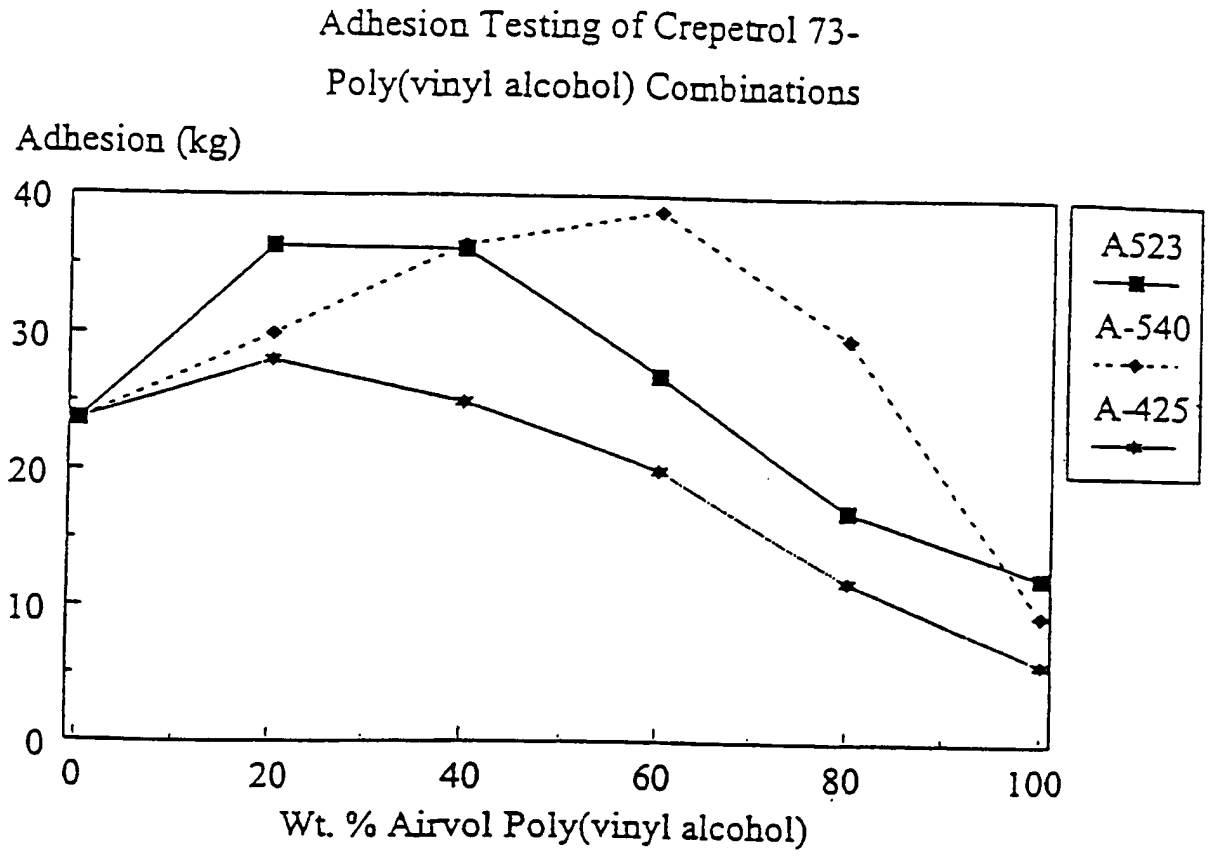


FIGURE 3


Adhesion Testing of Crepetrol 73-
Poly(vinyl alcohol) Combinations
Adhesion (kg)
40
30
20
10
0
0
20
40
60
80
100
Wt. % Airvol Poly(vinyl alcohol)
A523
A-540
A-425

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte ional Application No
PCT/US 00/31080

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4129528 A		GB 1537417 A	29-12-1978